

# VARIATIONAL CALCULATION OF THERMODYNAMIC PROPERTIES FOR $m-6-8$ POTENTIAL

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In Partial Satisfaction of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

By  
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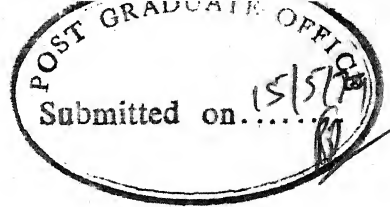
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# CERTIFICATE

It is certified that this work entitled 'Variational Calculation of Thermodynamic Properties for m-6-8 Potential' has been carried out by Mr. S. Michael Antony under my supervision and that this has not been submitted elsewhere for a degree.

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May 15, 1979

## POST GRADUATE OFFICE

This thesis has been approved  
for the award of the Degree of  
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## CHAPTER 1

### INTRODUCTION

Given a model potential, it is possible, atleast in principle, to obtain an equation of state from statistical thermodynamics and for this purpose many model potentials have been proposed starting with simple hard sphere potentials.

Several of these model potentials, like the hard sphere and Lennard-Jones potential, have been extensively studied. Virial coefficients and transport properties are evaluated directly from the potentials and thermodynamic properties through an equation of state. However, the hard sphere model and the L.J. potential give reasonably accurate results only for simple monatomic substances. But for polyatomic molecules they fail to give satisfactory results; some of the reasons for which are discussed in the latter chapters. Since we are concerned with polyatomic molecules in this thesis we are looking for a more representative model potential. The m-6-8 potential proposed by Hanley and Coworkers is one of the obvious choices for this purpose. A detailed discussion of this potential is presented in the next chapter.

Even if we have a good model potential, it would be of little consequence if an equation of state can not be obtained from that model. Most often this is the crux of the problem

and until this is achieved one does not really know which is a good model potential. Various thesis based on perturbation technique and variational methods are currently being tried out. The so-called computer experiments played a significant role in the development and assessment of the accuracy of these thesis.

Though the results of perturbation calculations have been satisfactory for a large number of potentials in a given temperature range, the mathematics involved in the expansion of the radial distribution function in powers of perturbation potentials are cumbersome. Often this series has to be terminated with the second order terms and the errors involved in this is significant at low temperatures or when attractive forces are important. But higher order perturbation theories are exceedingly complicated.

Hence in this work the variational method (discussed in detail in Chapter 4) is used to obtain an equation of state for the m-6-8 potential. Using the potential parameters applicable to pure  $\text{CO}_2$  the equation of state and the vapour liquid coexistence curve have been obtained and compared with experimental measured values. It is found that the agreement is quite satisfactory.

## CHAPTER 2

## m-6-8 POTENTIAL

2.1 Introduction

H.J.M. Hanley and Max Klein [1] of NBS, Washington, proposed a four parameter potential function based on the semi-theoretical m-6-8 potential.

The semi-theoretical potential is

$$\phi(r) = \frac{A}{r^m} - \frac{c_6}{r^6} - \frac{c_8}{r^8} \quad (2.1.1)$$

where A, m,  $c_6$  and  $c_8$  are some constants.

The model proposed by Hanley and Klein is

$$\phi(r) = \varepsilon \left[ \frac{6+2v}{m-6} (\sigma/r)^m d^m - \frac{m-v(m-8)}{m-6} (\sigma/r)^6 d^6 - v (\sigma/r)^8 d^8 \right] \quad (2.1.2)$$

In reduced form (2) becomes

$$\phi^*(r^*) = \frac{6+2v}{m-6} \left( \frac{1}{r^*} \right)^m - \frac{m-v(m-8)}{m-6} (1/r^*)^6 - v (1/r^*)^8 \quad (2.1.3)$$

In equations (2.1.1), (2.1.2) and (2.1.3)

(i)  $\sigma$  is defined by the condition  $\phi(\sigma) = 0$

(ii)  $d$  is the ratio of  $r_m$  and  $\sigma$

(iii)  $r_m$  is defined by  $\phi'(r_m) = 0$

(iv)  $\epsilon$  is given by  $\phi(r_m) = -\epsilon$

(v)  $\phi^* = \phi/\epsilon$

and

(vi)  $r^* = r/r_m = r/d\sigma$

The four parameters in this model are  $m$ ,  $v$ ,  $\epsilon$ , and  $\sigma$  (or  $\gamma_m$ ).

' $m$ ' represents the strength of the repulsion while  $v$  represents the strength of the inverse eighth power attraction between the molecules. In the following we will refer to (2.1.2) and (2.1.3) as the  $m$ -6-8 potential for simplicity.

## 2.2 Selection of Parameters for $m$ -6-8 Model

The four parameters  $m$ ,  $v$ ,  $\sigma$  and  $\epsilon/k$  are calculated either by fitting experimental viscosity data or from collision integral calculations. The former is simple but not accurate while the latter is comparatively more accurate but laborious.

Ely and Homley [2] used the two procedures simultaneously to optimise the time and accuracy. The actual details are described in ref. [2].

Normally  $v$  is selected for each  $m$  such that  $m - v(m-8) > 0$  while  $m$  is selected between 9 and 18. The following table provides parameters of the  $m$ -6-8 potential obtained by Ely and Hanley for some common gases.

TABLE 1

Gas	m	$\nu$	$\sigma(\text{\AA})$	$\epsilon/k$ ( $^{\circ}\text{K}$ )
Argon	11	3	3.292	153.0
Krypton	11	3	3.509	216.0
Xenon	11	3	3.841	295.0
Oxygen	10	1.0	3.450	109.5
Methane	11	3.0	3.680	168.0
Nitrogen	12	2.0	3.540	118.0
Carbondioxide	14	1.0	3.680	282.0

### 2.3 Applications of m-6-8 Potential and Results

This model potential had been applied to Argon, Krypton, Xenon, Nitrogen, Methane and Carbondioxide to check its 'utility and validity' [3]. Properties like viscosity coefficient, self diffusion coefficient, thermal conductivity, virial coefficients and the isotopic thermal diffusion factor were calculated and the results were found to be in excellent agreement with experimental values over a wide temperature range [3].

Caligaris and Rodriguez [4] calculated the reduced third virial coefficient for Argon assuming pairwise additivity with  $m = 11$ ,  $\sigma = 3.292 \text{ \AA}$ ,  $r_m = 3.667 \text{ \AA}$  and  $\epsilon/k = 153.0 \text{ }^{\circ}\text{K}$ . They compared the result of this calculation to the experimental

values of Argon and found a wide deviation between them. However, Hanley and McCarty [5] corrected their results using non-additive terms and found a good agreement with experimental results.

Thus the spherically symmetric m-6-8 model proves to be reasonable for non-spherical polyatomic molecules like Carbondioxide and Methane also. But to account for the orientation dependence in such molecules, angle dependent terms should be added as shown latter. Self diffusion coefficients of Methane were calculated using the molecular dynamic technique [6] for m-6-8 potential and agreement with the experimental data is within estimated errors. Collision integrals and dielectric second virial coefficients were evaluated for a non-spherical m-6-8 potential function for Carbondioxide [7]. Agreement between calculated and experimental values was 'generally satisfactory'.

These applications and their results show the capability of m-6-8 potential functions in the prediction of physical and transport properties for spherical as well as non-spherical molecules and encourage us to apply this model for the prediction of phase equilibrium properties.

#### 2.4 Superiority of the m-6-8 Model

The three parameter potentials such as Lennard-Jones potential may be compared to the m-6-8 model. The three parameter potential functions have three major limitations :

(i) A set of parameters selected to fit a property in a given temperature range cannot be generally relied upon to predict the property in some other temperature range.

(ii) A set of parameters which predict one kind of property do not predict another kind of property correctly.

(iii) The parameters do not always agree with values obtained from independent information such as scattering experiments.

On the other hand the m-6-8 potential has been used to correlate a given property over a wide temperature range and is able to predict properties of different types with a single set of parameters [3]. Thus the addition of the inverse eighth term to a three parameter function substantially improves the relation between theory and experiment and also with this addition, the limitations mentioned earlier are essentially removed. It is worth noting that the repulsive exponents in this model came out to be very close to the results of scattering experiments.

## 2.5 Weaknesses of m-6-8 Model

Though m-6-8 potential is an effective tool to handle simple monatomic gases, it is not free of limitations. The two important limitations of m-6-8 model are discussed below.

(i) Dispersion coefficients

From (2.1.1) and (2.1.2) the dispersion coefficients  $c_6$  and  $c_8$  are given by

$$c_6 = \frac{\epsilon}{m-6} (m - v (m-8)) d^6 \sigma^6 \quad (2.5.1)$$

$$c_8 = \epsilon v \sigma^8 d^8 \quad (2.5.2)$$

From (2.5.1) and (2.5.2), it is evident that dispersion coefficients are strong functions of  $\sigma$ ;  $\sigma$  is obtained from experiments and since  $\sigma$  is raised to sixth or eighth power, it can introduce considerable uncertainty in  $c_6$  and  $c_8$ .

To reduce this uncertainty, one immediate suggestion is that more parameters should be added to the model. This view can be considered by referring to a potential function due to Barker [8], in which he has added additional parameters to the repulsive term.

The m-6-8 potential with  $m = 11$  and  $v = 2$  is, however, very close to Barker's multiparameter potential for which  $c_6$  is fixed at the 'correct' value. It would thus appear that adding more parameters to m-6-8 potential would not necessarily remove the uncertainty. Instead of keeping  $c_6$  and  $c_8$  as constants for all the temperature and density conditions we can change them by varying the parameter  $\sigma$  to fit the properties effectively as is done in computer experiments, perturbation



theories and variational methods. Reference [15] provides a review of these methods.

## (ii) Anisotropic Forces

The spherically symmetric m-6-8 potential cannot be, strictly speaking applicable for polyatomic molecules as it does not include any angle dependent interactions. But in predicting phase equilibrium properties it has been shown by Gubbins and Gray [19] that the anisotropic part of the potential plays a crucial role. Near the critical point the calculated results prove to be very sensitive to the angle-dependent terms. In fact in systems that have a liquid-liquid-gas line that ends at an upper critical end point, which have been studied in detail by Gubbins [19] et al, it is found that anisotropic forces are perhaps the most decisive. Hence the effect of adding specific angle dependent interactions to the m-6-8 model may be expected to be significant. We carry out a preliminary study of these effects in  $\text{CO}_2$  in this thesis.

## 2.6 Anisotropic Potentials

The earlier works involving calculation of phase equilibrium properties used angle dependent potentials such as rigid ellipsoids of revolution, spherocylindrical molecular model (Kihara), rigid spheres containing a point

dipole (Keesom) and Stockmayer potential. The details of these potentials are given by Hirschfelder et al [20]. But these models consider only shape dependent terms, are not complete and cannot predict the properties correctly.

For polarizable, quadrupolar molecules such as  $\text{CO}_2$ ,  $\text{N}_2$  and  $\text{F}_2$ , we must consider the following general potential.

$$\phi(r) = \phi(\text{spherical}) + \phi(\text{quadrupole}) + \phi(\text{induced dipole}) \\ + \phi(\text{shape}) + \phi(\text{anisotropy})$$

The first term is the spherical contribution - the m-6-8 in our case, the second term represents the electrostatic interactions of the permanent quadrupole moments and the third term represents the induced-dipole interactions caused by the induction effect of the quadrupolar moments and when applicable, by the presence of an external electric field. Finally, the last two terms depict the anisotropy in the repulsive forces.

The last two terms may be neglected for the following reasons :

- (i) It is currently impossible to determine independently the parameters for the shape part of the potential.
- (ii) The anisotropic contributions have not been worked out in enough detail for m-6-8 potential.

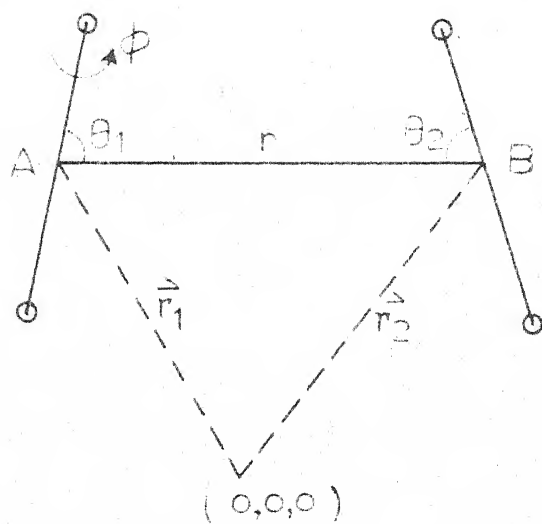


Fig. 1

(iii) The spherical potential does reasonably well and hopefully, therefore, incorporates part of these corrections into the spherical parameters, especially that of the shape.

With these assumptions the model potential is modified as :

$$\varphi = \phi_{m-6-8}(|\vec{r}|) + \phi_{quad}(\vec{r}, w_1, w_2) + \phi_{ind}(\vec{r}, w_1, w_2) \quad (2.6.1)$$

where  $w_i$  denotes the set of angles describing the orientation of the molecule  $i$  with respect to a space-fixed coordinate system and  $\vec{r}$  is a vector connecting the centres of mass of the two interacting molecules. The spherical term  $\phi_{m-6-8}(|\vec{r}|)$  is given by equation (2.1.2) with  $|\vec{r}| \equiv r$ .

It is always convenient for linear molecules to write out the anisotropic contribution to the potential in terms of the relative orientation of the two molecules given by  $(\theta_1, \theta_2, \phi)$  (see Fig. 1).

$r$  = distance between the centres of molecules 1 and 2.

$\theta_1, \theta_2$  = relative angles made by molecules 1 and 2 with  $r$ .

$\phi = \phi_1 - \phi_2$  = azimuthal angle of molecule 1 with respect to the plane containing  $r$  and molecule 2. In terms of  $r$ ,  $\theta_1$ ,  $\theta_2$  and  $\phi$  the last two terms in equation (6) become

$$\begin{aligned} \phi_{quad} = \frac{3\phi^2}{4r^5} [1 - 5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos^2 \theta_1 \cos^2 \theta_2 + \\ 2(4 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi)^2] \end{aligned} \quad (2.6.2)$$

and

$$\phi_{\text{ind}} = \frac{9\alpha\theta^2}{8r^8} (\sin^4\theta_1 + \sin^4\theta_2 + 4\cos^4\theta_1 + 4\cos^4\theta_2) \quad (2.6.3)$$

where  $\alpha$  is the mean polarizability and  $\theta$  is the scalar quadrupole moment.

Table 2 provides  $\alpha$  and  $\theta$  for  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  which are taken from references 2 and 3.

Table 2

Gas	$10^{26}\theta(\text{esu})$	$10^{24}\alpha(\text{cm}^3)$
Oxygen	$- 0.4 \pm 0.1$	1.568
Nitrogen	$- 1.4 \pm 0.1$	1.730
Carbondioxide	$- 4.3 \pm 0.2$	2.925

## CHAPTER 3

## VARIATIONAL METHOD

3.1 Introduction

The essential idea of the variational techniques is to expand the thermodynamic properties of the system about a simple reference system with a known relationship between its macroscopic and microscopic properties.

This idea is originally due to Zwanzig [21]. Using this method many works [22, 23] had been carried out based upon a simple system of hardspheres.

Ali Mansoori and Canfield improved the variational technique to calculate the equilibrium thermodynamic properties of simple fluids [24] and fluid mixtures [25]; they also extended it to apply to the melting process [26].

Their variational technique is based on an inequality pertaining to the Helmholtz free energy which is discussed below. Helmholtz free energy of the original system is calculated by variation around the free energy of the reference system based on the this inequality and the other thermodynamic properties are calculated from the free energy.

### 3.2 Inequality for the Helmholtz Free Energy

Let us consider a variable  $x$  which has a probability distribution function  $p(x)$ . Then the average of any function is defined as

$$\langle f(x) \rangle = \int p(x) f(x) dx$$

From Taylor series expansion of  $\langle f(x) \rangle$  around  $f(\langle x \rangle)$

$$\langle f(x) \rangle = f(\langle x \rangle) + \frac{\langle (x - \langle x \rangle)^2 \rangle}{2!} f''(\langle x \rangle) + \dots$$

The linear term in  $x - \langle x \rangle$  is absent since  $\langle x - \langle x \rangle \rangle = 0$ .

The above series gives the two following inequalities [27]

$$(i) \quad \langle f(x) \rangle \geq f(\langle x \rangle) \quad (3.2.1)$$

if  $f''(x) \geq 0$ .

$$(ii) \quad f(\langle x \rangle) \geq f(\langle x \rangle) + \frac{\langle (x - \langle x \rangle)^2 \rangle}{2!} f''(\langle x \rangle) +$$

$$\frac{\langle (x - \langle x \rangle)^3 \rangle}{3!} f'''(\langle x \rangle) \quad (3.2.2)$$

if  $f'''(x) \geq 0$

Let  $U$  be the potential energy of the original system and  $U_0$  be that of the reference system at the same temperature and density. Then at equilibrium, we have

$$f/f_0 = \langle \exp [-\beta(U - U_0)] \rangle_0 \quad (3.2.3)$$

where  $f_0$  and  $f_1$  are the partition functions of the reference and the original system respectively.

Equation (3.2.3) means that  $f/f_0$  is equal to the expectation value of  $\exp(-\beta(U-U_0))$  over the probability distribution function of the reference system,  $\exp(-\beta U_0)/z_0$  where  $z_0$  is the configurational integral of the reference system.

Substituting  $x = -\beta(U - U_0)$  (3.2.1) gives

$$f/f_0 \geq \exp(-\beta \langle U - U_0 \rangle_0) \quad (3.2.4)$$

and (3.2.2) gives

$$f/f_0 \geq \exp(-\beta \langle U - U_0 \rangle_0) \{ 1 + (\beta^2/2!)y_2 - (\beta^3/3!)y_3 \} \quad (3.2.5)$$

$$\text{where } y_2 = \langle (U - U_0 - \langle U - U_0 \rangle_0)^2 \rangle_0$$

$$\text{and } y_3 = \langle (U - U_0 - \langle U - U_0 \rangle_0)^3 \rangle_0$$

We know that the Helmholtz free energy  $A$  is given by

$$A = -kT \ln f \quad (3.2.6)$$

Substituting

$$A \leq A_0 + \langle U - U_0 \rangle_0 \quad (3.2.7)$$

and

$$A \leq A_0 + \langle U - U_0 \rangle_0 - kT \ln (1 + \frac{1}{2} \beta^2 y_2 - \frac{1}{6} \beta^3 y_3) \quad (3.2.8)$$



Inequality (3.2.8) contains  $y_2$  and  $y_3$  which are functions of second and higher order correlation functions of the reference system which are exceedingly complicated [27]. Further in a thermodynamic system with  $N$  particles (of the order  $10^{23}$ , the first and second terms in the RHS of (3.2.8) are of the order of  $NkT$  while the third term is of the order of  $kT \ln(N)$ . Consequently inequality (3.2.8) will be practically the same as inequality (3.2.7). Ali Mansoori et al calculated the Helmholtz free energy using (3.2.8) with great difficulty and found that the result is not improved even slightly compared to that obtained from (3.2.7) but led to some errors. [24]. Hence in this work, inequality (3.2.7) is used for further calculations.

### 3.3 Representation of $\langle U - U_0 \rangle_0$ in terms of m-6-8 and hardsphere Potentials

$\langle U - U_0 \rangle_0$  in (3.2.7) can be expressed in terms of the m-6-8 potential function by considering only two body interactions as follows :

$$U = \sum_{i < j = 1}^N \phi_{ij}(r_{ij}, \Omega_{ij})$$

and

$$U_0 = \sum_{i < j = 1}^N \phi_{oij}(r_{ij})$$

For any property  $x$ ,

$$\langle x \rangle_0 = \frac{1}{K} \iiint \dots \int (\exp(-\beta U_0)/Z_0) x \, dr_1 \, dr_2 \dots dr_N \, d\Omega_{12} \, d\Omega_{13} \dots d\Omega_{(N-1)N}$$

Therefore,

$$\langle U - U_0 \rangle_0 = \frac{1}{K} \iiint \dots \int (\exp(-\beta U_0)/Z_0) (U - U_0) \, dr_1 \, dr_2 \dots dr_N \, d\Omega_{12} \, d\Omega_{13} \dots d\Omega_{(N-1)N} \quad (3.3.1)$$

where  $k$ , and  $K$  are normalization constants and  $d\Omega_{ij}$  is given by

$$d\Omega_{ij} = \sin\theta_i \, d\theta_i \, \sin\theta_j \, d\theta_{ij} \quad (3.3.2)$$

$Z_0$ , the configurational integral of the reference system is given by

$$Z_0 = \int \dots \int \exp(-\beta U_0) \, dr_1 \, dr_2 \dots dr_N.$$

Separating the angle dependent terms in (3.3.1),

$$\begin{aligned} \langle U - U_0 \rangle_0 &= \frac{1}{K} \int \dots \int \frac{1}{Z_0} \exp(-\beta \sum_{i < j=1}^N \phi_0(r_{ij})) \, dr_1 \, dr_2 \dots dr_N \times \\ &\dots \sum_{i < j=1}^N (\phi_{ij} - \phi_{0ij}) \, d\Omega_{12} \, d\Omega_{13} \dots d\Omega_{(N-1)N} \quad (3.3.3) \end{aligned}$$

Now the angle dependent part can be integrated over all angles to give

$$\begin{aligned} \langle U - U_0 \rangle_0 = \frac{1}{K_1} \{ \int \dots \int \frac{1}{Z_0} \exp(-\beta \sum_{i < j=1}^N \phi_0(r_{ij})) dr_1 dr_2 \\ \dots dr_N \} \{ \sum_{i < j} \psi(r_{ij}) - 8\pi \phi_0(r_{ij}) \} \end{aligned} \quad (3.3.4)$$

where the integral of the m-6-8 potential along with angle dependent terms (as in equation (3.3.4)) over  $dr_{ij}$  is defined as  $\psi(r_{ij})$ . Since  $\phi_0(r_{ij})$  is independent of  $r_{\Omega}$ , integration with respect to  $\Omega_{ij}$  will give  $8\pi \phi_0(r_{ij})$ . Note that  $K_1 = 8\pi$  and is different from  $K$ .

The radial distribution function  $g^0$  for the reference system is given in terms of second order correlation function as

$$\begin{aligned} g^0(r) &= \frac{f_2}{\rho^2} \\ &= \frac{N(N-1)}{\rho^2 Z_0} \int \dots \int \exp(-\beta U_0) dr_3 dr_4 \dots dr_N \end{aligned} \quad (3.3.5)$$

Representing the integral (3.3.4) by relative vector  $r_{12}$  etc.,

$$\begin{aligned} \langle U - U_0 \rangle_0 &= \frac{1}{8\pi} \frac{N(N-1)}{2} \int \frac{1}{Z_0} [\exp(-\beta U_0)] [\psi(r_{12}) \\ &\quad - 8\pi \phi_0(r_{12})] dr_1 dr_2 \dots dr_N \end{aligned} \quad (3.3.6)$$

Combining (3.3.5) and (3.3.6)

$$\begin{aligned} \langle U - U_0 \rangle_0 &= \frac{2}{16\pi} \int_V g_0(r_{12}) [\psi(r_{12}) - 8\pi \phi_0(r_{12})] dr_1 dr_2 \\ &= \frac{N^2}{4V} \int g_0(r) r^2 [\psi(r) - 8\pi \phi_0(r)] dr \end{aligned} \quad (3.3.7)$$

where

$$[\psi(r) - 8\pi\phi_0(r)] = \int_{\Omega} [\phi(r, \Omega) - \phi_0(r)] d\Omega \quad (3.3.8)$$

and  $V$  is the volume.

Combining (3.3.7) and (3.3.8)

$$\begin{aligned} \langle U - U_0 \rangle_0 &= \frac{N^2}{4V} \int_0^{\infty} r^2 g_0(r) dr \int_{\Omega} [\phi(r, \Omega) - \phi_0(r)] d\Omega \\ &= \frac{N^2}{4V} \int_0^{\infty} r^2 g_0(r) \int_0^{\pi} \sin\theta_1 d\theta_1 \int_0^{\pi} \sin\theta_2 d\theta_2 \\ &\quad \int_0^{2\pi} d\phi [\phi(r, \Omega) - \phi_0] \end{aligned} \quad (3.3.9)$$

Taking the last integral from (3.3.9)

$$\begin{aligned} &\int_0^{2\pi} [\phi(r, \Omega) - \phi_0(r)] d\phi \\ &= \int_0^{2\pi} \{ [\phi_{sp}(r) - \phi_0(r)] + \frac{3\theta^2}{4r^5} (1 - 5 \cos^2\theta_1 - 5 \cos^2\theta_2 - \\ &\quad - 15 \cos^2\theta_1 \cos^2\theta_2 + 2(4\cos\theta_1 \cos\theta_2 \\ &\quad - \sin\theta_1 \sin\theta_2 \cos\phi)^2) - \frac{29\alpha\theta^2}{8r} (\sin^4\theta_1 + \sin^4\theta_2) \\ &\quad + 4 \cos^4\theta_1 + 4 \cos^4\theta_2 \} d\phi \\ &= 2\pi(\phi_{sp} - \phi_0) + \frac{3}{2} \frac{\pi\theta^2}{r^5} (1 - 5 \cos^2\theta_1 - 5 \cos^2\theta_2 - 15 \cos^2\theta_1 \\ &\quad \cos^2\theta_2) \end{aligned}$$

$$+ \frac{48\pi\theta^2}{r^5} \cos^2\theta_1 \cos^2\theta_2 + \frac{3\pi\theta^2}{2r^5} \sin^2\theta_1 \sin^2\theta_2$$

$$- \frac{9\alpha\theta^2}{4r^8} (\sin^4\theta_1 + \sin^4\theta_2 + 4 \cos^4\theta_1 + 4 \cos^4\theta_2)$$

Now,

$$\int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi(\phi(r, \Omega) \phi_0(r))$$

$$= 4\pi(\phi_{sp} - \phi_0) + \frac{3\pi\theta^2}{2r^5} (2 - 10 \cos^2\theta_1 - \frac{10}{3} - 10 \cos^2\theta_1)$$

$$+ \frac{32\pi\theta^2}{r^5} \cos^2\theta_1 + \frac{2\pi\theta^2}{r^5} \sin^2\theta_1 - \frac{9\pi\alpha\theta^2}{4r^8} (2 \sin^4\theta_1$$

$$+ \frac{16}{15} + 8 \cos^4\theta_1 + \frac{8}{5})$$

and finally

$$\int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi[\phi(r, \Omega) - \phi_0(r)]$$

$$= 8\pi(\phi_{sp} - \phi_0) - \frac{24\pi\alpha\theta^2}{r^8} \quad (3.3.10)$$

Equation (3.3.10) contains no quadrupole interaction term since it vanishes when averaged over all the orientations. But in real systems of  $\text{CO}_2$ , the effect of quadrupole interaction is not negligible and hence this seems to be a weakness of this

approach. The dipole moment of  $\text{CO}_2$  is zero and hence no dipole interaction term is included. Even if a system has dipole interaction, the unweighted average of it over all the orientations will also vanish as in the case of quadrupole interactions.

This is because in this method only the unweighted average of the potential enters the inequality. Physically, however, the molecules will tend to spend more time in those orientations which give the lowest energy. The average potential in these cases may be taken as

$$\bar{\phi}_{\text{quad}} = \frac{\iint \phi_{\text{quad}} [\exp(-\phi_{\text{quad}}/kT)] dw_1 dw_2}{\iint [\exp(-\phi_{\text{quad}}/kT)] dw_1 dw_2} \quad (3.3.11)$$

(3.3.11) cannot be easily evaluated analytically and hence (3.3.10) is taken for further calculations.

Combining (3.3.9) and (3.3.10)

$$\langle U - U_0 \rangle_0 = \frac{2\pi N^2}{V} \int_0^\infty g_0(r) r^2 [(\phi_{\text{sp}} - \phi_0) - \frac{3\alpha \theta^2}{r^8}] dr \quad (3.3.11)$$

Substituting (3.3.11) in (3.2.7) we have

$$A < A_0 + \frac{2\pi N^2}{V} \int_0^\infty g_0(r) r^2 [(\phi_{\text{sp}} - \phi_0) - \frac{3\alpha \theta^2}{r^8}] dr \quad (3.3.12)$$

Defining the nondimensional A as

$$A^* = A/NkT$$

(3.3.12) gives

$$A^* \leq A_0 + \frac{2\pi\rho}{kT} \int_0^{\infty} (\phi_{sp} - \phi_0 - \frac{3\alpha\theta^2}{8r}) g_0(r) r^2 dr \quad (3.3.13)$$

Considering the hard sphere reference system,

$$\begin{aligned} \phi_0 &= 0 & \text{for } r \geq 1 \\ &= \infty & \text{for } r < 1 \end{aligned}$$

and

$$g_0(r) = 0 \quad \text{for } r < 1$$

where 1 is the hard sphere diameter. Using the above equations of hard sphere system, (3.3.13) becomes

$$A^* \leq A_0^* + 2\pi\rho\beta \int_1^{\infty} (\phi_{sp} - \frac{3\alpha\theta^2}{8r}) g_0(r) r^2 dr \quad (3.3.14)$$

Nondimensionalising  $r$  by defining

$$x = r/1$$

(3.3.14) becomes

$$A^* \leq A_0^* + 2\pi\beta l^3 \int_1^{\infty} (\phi_{sp} - \frac{3\alpha\theta^2}{8r}) g_0(x) x^2 dx \quad (3.3.15)$$

Let us introduce the variational parameter 'c' defined as

$$c = 1/\sigma$$

$\phi_{sp}$  (m-6-8 potential) as a function of  $x$  with the parameter  $c$  is given by

$$\phi_{sp}(x) = \varepsilon [c_m (1/cx)^m - c_6 (1/cx)^6 - (1/cx)^8] \quad (3.3.16)$$

where

$$c_m = \frac{6 + 2v}{m - 6} d^m$$

$$c_6 = \frac{m - v(m-8)}{m - 6} d^6$$

and

$$c_8 = v d^8$$

With this equation (3.3.15) becomes

$$\begin{aligned} A^* \leq A_O^* + 2\pi \rho \beta l^3 \int_1^\infty \{ [\varepsilon (c_m (1/cx)^m - c_6 (1/cx)^6 - c_8 (1/cx)^8)] \\ - \frac{3\alpha\theta^2}{(cx\sigma)^8} g_0(x) x^2 dx \} \end{aligned} \quad (3.3.17)$$

Let us define

$$V(x) = [c_m (1/cx)^m - c_6 (1/cx)^6 - c_8 (1/cx)^8 - \frac{3\alpha\theta^2}{\varepsilon\sigma^8} (1/cx)^8]$$



$$A^* \leq A_0^* + 2\pi \rho \beta \frac{1}{3} \epsilon \int_1^{\infty} V(x) g_0(x) x^2 dx \quad (3.3.18)$$

Now the concern is with  $g_0(x)$  for a hard sphere system. Many methods are available to evaluate  $g_0(x)$  analytically and numerically [28] - [32]. Except Wertheim's analytical expression [28], all the others are either numerical or in the form of complicated integrals which cannot be used conveniently in the variational calculations.

Wertheim [28] has obtained the explicit Laplace transform  $G(s)$  of the hard sphere  $g_0(r)$  satisfying Percus-Yevick integral equation

$$G(s) = \int_1^{\infty} \exp(-sx) g_0(x) x dx \quad (3.3.19)$$

$g_0(r)$  obtained from (3.3.19) has two main defects [36] when compared with Monte-Carlo or molecular dynamic simulation results.

(i) It predicts a low first peak. This can be corrected by defining a new value for  $\sigma$ . But in this work as  $\sigma$  is included in the variational parameter 'c', this correction is not necessary.

(ii) It does not predict the consecutive peaks and oscillations properly. To correct this an additional increment  $dg(x)$  should be added. We assume that this error does not significantly affect the calculation of the thermodynamic properties.

Hence (3.3.19) is used in this work without any addition of extra terms.

Defining the nondimensional temperature

$$T^* = 1/\beta \varepsilon$$

(3.3.18) becomes

$$A^* \leq A_0^* + \frac{2\pi \rho l^3}{T} \int_1^\infty V(x) g_0(x) x^2 dx \quad (3.3.20)$$

Let us consider  $V(s)$  as the Laplace inverse of  $x V(x)$ ; then

$$x V(x) = \int_0^\infty \exp(-sx) V(s) ds \quad (3.3.21)$$

Substituting (3.3.21) in (3.3.19) and arranging the integrals,

$$x V(x) g_0(x) x dx = \int_0^\infty V(s) G(s) ds \quad (3.3.22)$$

(3.3.20) and (3.3.22) give

$$A^* \leq A_0^* + \frac{2\pi \rho l^3}{T} \int_0^\infty V(s) G(s) ds \quad (3.3.23)$$

$$V(s) = L^{-1} [x V(x)]$$

$$= c_m (1/c)^m \frac{s^{m-2}}{(m-2)!} - c_6 (1/c)^6 \frac{s^4}{4!} - c_8 (1/c)^8 \frac{s^6}{6!} - \frac{3\alpha\theta^2}{\varepsilon\sigma^8} (1/c)^8 \frac{s^6}{6!} \quad (3.3.24)$$

and

$$G(s) = L[x g_0(x)]$$

From Wertheim [28]

$$G(s) = s L(s)/12\eta[L(s) + S(s) e^s] \quad (3.3.25)$$

where

$$L(s) = 12\eta[(1 + \frac{1}{2}\eta)s + (1 + 2\eta)] \quad (3.3.26)$$

$$S(s) = (1 - \eta)^2 s^3 + 6\eta(1-\eta)s^2 + 18\eta^2 s - 12\eta(1 + 2\eta) \quad (3.3.27)$$

and

$$\begin{aligned} \eta &= \frac{1}{6} \pi \rho l^3 \\ &= \frac{1}{6} \pi \rho \sigma^3 c^3 \\ &= \frac{1}{6} \pi \rho^* c^3 \end{aligned}$$

where  $\rho^* = \rho \sigma^3$  is the nondimensional number density. Now (3.3.23) can be written as

$$A^* \leq A_0^* + \frac{12\eta}{T^*} \int_0^\infty V(s) G(s) ds \quad (3.3.28)$$

For a single component thermodynamic system, according to phase rule, if two of the intensive properties of the system are given, the other properties will be defined. Of course,

along the phase transition line one intensive thermodynamic variable of the system will be enough to fix the other variables. Then in general if we choose the two independent variables , the density and  $T$ , the temperature, one could write,

$$A = A(\rho, T)$$

and the inequality (3.3.28) becomes

$$A^*(\rho^*, T^*) \leq A_O^*(\rho^*, T^*, c) + \frac{1}{T^*} F(\rho^*, c) \quad (3.3.29)$$

where

$$F(\rho^*, c) = 12\eta \int_0^\infty V(s) G(s) ds$$

The RHS of (3.3.29) is a function of  $\rho^*$ ,  $T^*$  and  $c$  whereas the LHS is only a function of  $\rho^*$  and  $T^*$ . This means, that, to bring the inequality (3.3.22) closer to equality, RHS should be required to satisfy the following conditions :

$$\frac{\partial A_O^*}{\partial c} + \frac{1}{T^*} \frac{\partial F}{\partial c} = 0 \quad (3.3.30)$$

$$\frac{\partial^2 A_O^*}{\partial c^2} + \frac{1}{T^*} \frac{\partial^2 F}{\partial c^2} \geq 0 \quad (3.3.31)$$

If these conditions are satisfied, there will be a relative minimum for the RHS of the inequality (3.3.29) with respect to  $c$  and (3.3.29) becomes

$$A^* (\rho^*, T^*) \approx [A_O^* (\rho^*, T^*, c) + \frac{1}{T} F(\rho^*, c_i)]_{c=c_{\min}} \quad (3.3.32)$$

where  $c_{\min}$  is the value of  $c$  which satisfies the condition (3.3.30) and (3.3.31).

## CHAPTER 4

CALCULATIONS FOR CO<sub>2</sub>4.1 Properties of the Hard sphere System

For hard sphere system, there are several equation of state available [34]. The Percus-Yevick equation [35, 36] is very simple and is in good agreement with machine calculated data. According to P-Y equation

$$\frac{PV}{NkT} = (1 + \eta + \eta^2 - \frac{3}{2}\eta^3)/(1 - \eta)^3 \quad (4.1.1)$$

(4.1.1) will give the Helmholtz free energy from the thermodynamic relation

$$\frac{A_o}{NkT} = \int_0^{\rho} \rho^{-1} \left( \frac{PV}{NkT} - 1 \right) d\rho + \ln \rho \rho^3 - 1 \quad (4.1.2)$$

and from (4.1.1) and (4.1.2)

$$\frac{A_o}{NkT} = A_o^* = \frac{1}{2} \ln (1-\eta) + \frac{3}{1-\eta} + \frac{3}{4} \left( \frac{1}{(1-\eta)^2} \right) - \frac{19}{4} \ln \rho \rho^3 \quad (4.1.3)$$

which will give the free energy of the reference system.

4.2 Calculations for CO<sub>2</sub>

For spherically symmetric m-6-8 model, the following parameters are selected for CO<sub>2</sub> (from table 1).

$m = 14$ ,  $v = 1.0$ ,  $\sigma = 3.68 \text{ \AA}$ ,  $\epsilon/k = 282 \text{ }^\circ\text{K}$  and  $d = 1.048729$

Substituting these values in (3.3.24) with proper units,

$$V(s) = 4.06395 \times 10^{-9} s^{12} c^{-14} - 0.00206393 s^6 c^{-8} - 0.055433 s^4 c^{-6} \quad (4.2.1)$$

(4.2.1) is true only if  $Q-Q$  interactions are excluded.

Hanley [7] found the following values are the best for  $CO_2$  systems when  $Q-Q$  interactions are also included.

$m = 11$ ,  $v = 0.5$ ,  $\sigma = 3.775 \text{ \AA}$ ,  $\epsilon/k = 217 \text{ }^\circ\text{K}$  and  $d = 1.1259862$

In the following, since we want to include the effect of  $Q-Q$  interactions the above values will be used. With this set of values (4.2.1) becomes

$$V(s) = 1.4230781 \times 10^{-5} s^9 c^{-11} - 1.976783 \times 10^{-3} s^6 c^{-8} - 0.1613395 s^4 c^{-6} \quad (4.2.3)$$

To simplify the calculations, let us substitute

$$A = V(s) \quad (\text{from (4.2.3)})$$

$$B = [(1 + \frac{1}{2}\eta) s + (1 + 2\eta)] 6\eta$$

and

$$D = [(1 + \frac{1}{2}\eta) s + (1 + 2\eta)] 12\eta + [1 - \eta]^2 s^3 + 6\eta (1-\eta)s^2 + 18\eta^2 s - 12\eta (1+2\eta)] e^s$$

Now (3.3.28) becomes

$$A^* \leq A_O^* + \frac{2}{T^*} \int_0^{\infty} \frac{AB}{D} ds \quad (4.2.4)$$

$A_O^*$  is given by (4.1.3). Differentiating  $A_O^*$  with respect to  $c$

$$\begin{aligned} \frac{\partial A_O^*}{\partial c} &= \frac{\partial A_O^*}{\partial \eta} \cdot \frac{\partial \eta}{\partial c} \\ &= \frac{(2 - \eta - \frac{1}{4} \eta^2)}{(1 - \eta)^3} (\pi \rho^* c^2) \end{aligned}$$

The condition (3.3.30) becomes

$$\frac{2 - \eta - \frac{1}{4} \eta^2}{(1 - \eta)^3} (\pi \rho^* c^2) + \frac{2}{T^*} \int_0^{\infty} \frac{1}{D^2} [D^2 A \frac{dB}{dC} + B \frac{dA}{dC}] - AB \frac{dD}{dC} ds = 0 \quad (4.2.5)$$

where

$$\begin{aligned} \frac{dA}{dC} &= -15.653859 \times 10^{-5} s^9 c^{-12} + 15.814264 \times 10^{-3} s^6 c^{-9} \\ &\quad + 0.968037 s^4 c^{-7} \end{aligned} \quad (4.2.6)$$

$$\frac{dB}{dC} = 3\pi \rho^* c^2 (1 + s + 4\eta + 5\eta) \quad (4.2.7)$$

$$\begin{aligned} \frac{dD}{dC} &= \pi \rho^* c^2 (6 + 6s - 6e^s + 3s^2 e^s - s^3 e^s) + 6\pi \eta \rho^* c^2 (4 + s - 4e^s + \\ &\quad + 3s e^s - s^2 e^s + \frac{s^3}{6} e^s) \end{aligned} \quad (4.2.8)$$

The integral in (4.2.5) cannot be evaluated analytically after substituting (4.2.6), (4.2.7) and (4.2.8) and hence it was evaluated numerically.

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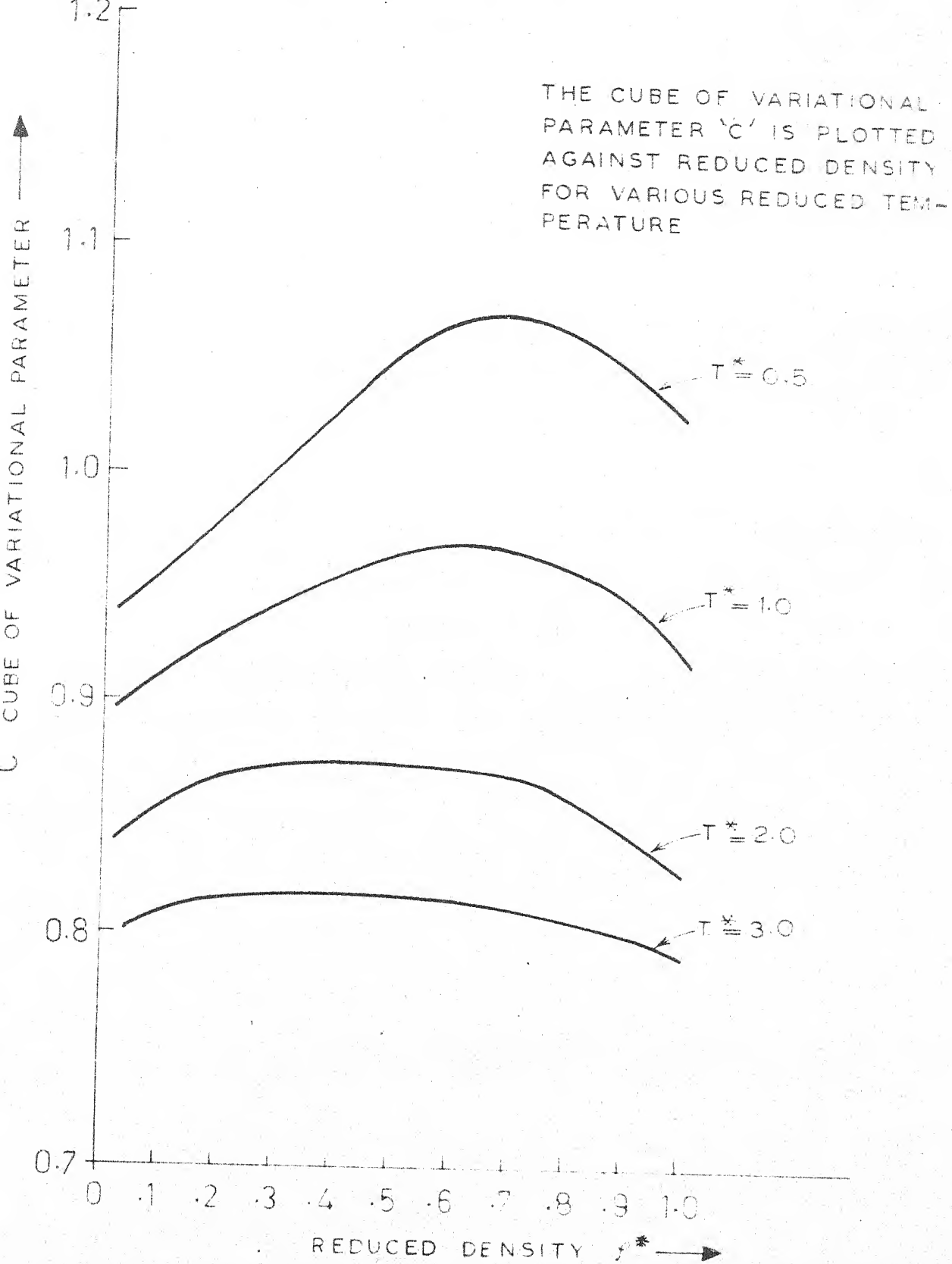


Fig. 2 Variational parameter

(i) The Helmholtz free energy

The inequality (4.2.4) will give the Helmholtz free energy when the integral of RHS is minimized; this integral has to be evaluated numerically. Similarly the integral in (4.2.5) has to be evaluated numerically to find the  $c$  which satisfies this equation. That particular  $c$  (which is  $c_{\min}$ ) should be substituted into (4.2.4) to get the 'correct' Helmholtz free energy for a particular temperature and density condition.

It is very difficult to check the condition (3.3.31) which involves the second derivative of  $A^*$  with respect to ' $c$ '. But it can be verified indirectly. The ' $c$ ' which satisfies the condition (3.3.30), (equation (4.2.5)), may either give maximum or minimum value of  $A^*$ , can be evaluated from (4.2.4) and (4.2.5). From the trend of the curve ' $A^*$ ' versus ' $c$ ' in the neighbourhood of  $c_{\min}$ , one can immediately conclude whether  $c_{\min}$  gives a maximum or minimum.

By evaluating the values of variational parameter ' $c$ ' which give the minimum value of  $A^*$ , it is evident that there is only one such ' $c$ ' for every  $T^* + \rho^*$ . In other words, RHS of (4.2.4) has only one minimum with respect to ' $c$ '.

The effect of temperature is studied from the calculation. It is found that at high temperatures, the variational parameter which is the ratio of hard sphere cut off diameter ' $\lambda$ ' to ' $\sigma$ ' is nearly unity (0.93 to 0.99) and it is also found that at there

temperature the ratio is almost independent of density.

But at very low temperatures, well below the critical temperature the ratio is found to be a strong function of density. Also the deviation from unity is more compared to the high temperature and the values are found to be greater than unity.

This shows that there is great deviation from the hard-sphere behaviour at very high temperatures because, when low energy collisions occur, the interacting system is strongly subject to the potential well. This fact is well established by Hirsch fields through quantum mechanical calculations.

The integrals in all these equations have limits zero to infinity and hence when they are evaluated, a convergence criterion should be considered for each thermodynamic condition to get the upper limit. The lower limit also gives computational troubles. When the variable  $s$  takes the values near zero, either under or overflow occurs.

In this work, these difficulties were minimized by using Gauss-Laguerre integration method by fitting the curve to a polynomial having 14 zeros. This method seems to be more accurate than Simpson's method with reasonably small increment in  $s$ . Further, computational time is found to be less than 1/100th of the required for Simpson's method when the increment used in the latter method is such that it gives the same result as the former method.

Using these values of  $c_{\min}$  values of  $A^*$  are obtained for various sets of nondimensional temperature ( $T^*$ ) and nondimensional density ( $\rho^*$ ).

(ii) Equation of State

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = -P \quad (4.2.9)$$

We know that

$$\left(\frac{\partial A}{\partial V}\right)_{T,N} = \left(\frac{\partial A}{\partial \rho}\right)_{T,N} \left(\frac{\partial \rho}{\partial V}\right)_{T,N} \quad (4.2.10)$$

and

$$\rho = N/V \quad (4.2.11)$$

Therefore

$$\left(\frac{\partial \rho}{\partial V}\right)_{T,N} = -\rho^2/N \quad (4.2.12)$$

Substituting (4.2.12) in (4.2.10) and combining (4.2.9)

$$\left(\frac{\partial A}{\partial \rho}\right)_{T,N} \frac{\rho}{N} = P$$

Multiplying both sides by  $V/NkT$ ,

$$\left(\frac{\partial A^*}{\partial \rho^*}\right)_{T,N} = \frac{PV}{NkT} = Z \quad (4.2.13)$$

As  $\rho^* = \rho \sigma^3$ , (4.2.13) becomes

$$Z = \rho^* \left(\frac{\partial A^*}{\partial \rho^*}\right)_{T,N} \quad (4.2.14)$$

Equation (4.2.14) shows that the product of  $\rho^*$  with the differential coefficient of  $A^*$  with respect to  $\rho^*$  will give the compressibility factor.

We have evaluated  $\frac{\partial A^*}{\partial \rho^*}$  numerically for various  $\rho^*$  and  $T^*$ . For this purpose, fourth order difference method is used and is found to be very accurate. The derivative is evaluated continuously as a function of  $\rho^*$  with a regular interval and also at discrete points. The second method is less time consuming and the accuracy is adjustable without any loss of computer time. Compressibility isotherms have been evaluated for wide range of temperatures and graphs are drawn for some selected temperatures and are shown in Fig. 3 and Fig. 4 and also are given in Table 3.

The pressures calculated from this equation of state are compared with experimental result in Fig. 5 and the agreement is found to be good. At high temperatures the error is well within 5 percent for practical pressure range. However, at very high pressure, the error even exceeds 5 percent. But, it is to be mentioned that at all densities and temperatures, the prediction of this method are more accurate [38, 39] than the previous methods using LJ model. The spherical m-6-8 potential calculations are also compared with these results in Fig. 5 and it is found that the results obtained with the inclusion of dispersion on terms are better at 375°C.

## (iii) Phase equilibrium calculations

When two phases are at equilibrium, the temperatures, the pressures and the chemical potentials of the two phases should be equal. Considering the liquid and vapour phases, we have

$$P_L = P_V \quad (4.2.15)$$

$$(A+PV)_L = (A+PV)_V \quad (4.2.16)$$

Defining the nondimensional pressure as

$$P^* = \frac{P\sigma^3}{\epsilon} \quad (4.2.17)$$

Condition (4.2.15) becomes

$$P_L^* = P_V^* \quad (4.2.18)$$

Dividing (4.2.16) by  $NkT$ ,

$$(A^* + Z)_L = (A^* + Z)_V \quad (4.2.19)$$

$P$  can be related to  $Z$  as

$$P^* = Z \rho^* T^* \quad (4.2.20)$$

For a particular temperature we have  $A^*$ ,  $Z$  and hence  $P^*$  as a function of  $\rho^*$ . In the system of two equations (4.2.18) and (4.2.19), the only unknowns are the two densities of the co-existing phases which can be numerically solved using the calculated values of  $A^*$  and  $P$  for a particular  $T^*$  as a function  $\rho$ .

At low densities, the interval in  $P^*$  is not sufficiently close to get a reasonably accurate solution to the system of equations (4.2.18) and (4.2.19) and hence the interval which gives accurate solution for higher density range should be further divided into subintervals for low density range. As our interest is mainly on the critical region, the phase equilibrium calculations are carried out near the critical point and a plot of temperature versus co-existing densities of liquid and vapour is made as shown in Fig. 7. The logarithm of the vapour pressure predicted from this procedure is also plotted against inverse  $T^*$  as shown in Fig. 8.

The phase equilibrium and vapour pressure calculations prove that this method is quite satisfactory near the critical region. The phase equilibrium curves as shown in Fig. 7 are very close to the curves using the law of rectilinear diameter and the experimental values. While the saturated vapour locus is predicted with negligible error, the saturated liquid locus is predicted with a maximum error of about 6 percent.

It may be anticipated that the errors in these calculations will be reduced considerably if one takes the quadrupole interaction into account by taking the weighted average of this interaction over all the orientations. It is suspected that quadrupole interactions may play an appreciable part in the interaction between  $\text{CO}_2$  molecules [43].

Another improvement can be made in these calculations by taking a better reference system. When the reference system approaches the original system, the inequality (4.2.4) will tend to an equality.

(iv) Other thermodynamic properties

Thermodynamic properties like entropy, enthalpy and internal energy can be readily evaluated from  $A$  and  $Z$  which are already evaluated.

From thermodynamic relations,

$$\left( \frac{\partial A}{\partial T} \right)_{V,N} = -S$$

From the definition of  $A^*$ ,

$$A = A^* - NkT,$$

$$\frac{\partial A}{\partial T} = \frac{\partial A^*}{\partial T} - Nk = -S \quad (4.2.21)$$

Defining  $S^* = S/Nk$ ,

$$-S^* = T^* \frac{\partial A^*}{\partial T} + A^* \quad (4.2.22)$$

Internal energy  $U$  can be related to  $A$  by,

$$U = A + TS \quad (4.2.23)$$

Dividing by  $NkT$  on both sides and defining

$$U^* = A^* + S^* \quad (4.2.24)$$



Combining (4.2.22) and (4.2.24)

$$U^* = -T^* \frac{\partial A^*}{\partial T^*} \quad (4.2.25)$$

and from (4.2.24)

$$S^* = U^* - A^* \quad (4.2.26)$$

From the equations (4.2.25) and (4.2.26)  $U^*$  and  $S^*$  can be evaluated.

The nondimensional enthalpy  $H^*$  is defined by

$$H^* = H/NkT \quad (4.2.27)$$

and from the thermodynamic relation

$$H^* = A + PV + TS \quad (4.2.28)$$

We get

$$H^* = A^* + Z + S^* \quad (4.2.29)$$

Equation (4.2.29) will give one  $H^*$  for each value of  $\mu^*$  and  $T^*$ .

## CHAPTER 5

## CONCLUSION

The pressures calculated from this equation of state are compared with experimental results (Fig. 3,4 and 5) and the agreement is found to be good. At high temperatures there is negligible error and at low temperatures the error is well within 5 percent for practical pressure range.

The phase equilibrium and the vapour pressure calculations (Fig. 7 and 8) prove that this method is excellent near critical region. While the saturated vapour locus is predicted without any error, the saturated liquid locus is predicted with a maximum error of 6 percent.

The error in the liquid locus and in the values of pressures at low temperatures lead to two conclusions : (i) The quadrupole interaction term becomes zero in our calculations because only the unweighted average of the quadrupole moment term is considered. This has been already discussed in the calculation part. The absence of the quadrupole interaction term in the equation of state affects these calculations much at low temperatures and at higher pressures. It is suspected that the quadrupole interaction may play an appreciable in the interaction between  $\text{CO}_2$  molecules at low temperature and high pressure [41], (ii) The simple and

angle dependent hard sphere potential is taken as the reference system but on the otherhand the original system is angle dependent and containing more terms. Owing to this inadequency of the reference system, we can not expect the inequality for Helmholtz free energy, from which all the calculations are made, will tend to an equality even at the minimum value of  $A$  .

The spherical m-6-8 potential calculations with the best value available for m are compared with this calculations. It is also compared with L.J. potential calculations. It is concluded that this work leads to better results than the other two at all the thermodynamic conditions. Hence we can conclude that the addition of angle dependent terms improves the accuracy in the calculation of thermodynamic properties and gives satisfactory results.

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Table 3

Relation between dimensional and nondimensional PVT

Property	Relation to non-dimensional property	Relation for carbondioxide
1. Temperature in $^{\circ}\text{K}$	$T = \frac{\epsilon}{k} T^*$	$T = 217 T^*$
2. Pressure in atmospheres	$P = \frac{\epsilon}{\sigma^3} P^*$	$P = 549.378 P^*$
3. Density in gm/cc	$\rho = \frac{\bar{M}}{\bar{N} \sigma^3} \rho^*$	$\rho = 1.3579661 \rho^*$

PVT data for CO<sub>2</sub>

$$T^* = 0.1$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	-0.00045	0.52	-2.01660
0.04	-0.00545	0.54	-2.18110
0.06	-0.01551	0.56	-2.34990
0.08	-0.03086	0.58	-2.52232
0.10	-0.05173	0.60	-2.69764
0.12	-0.07835	0.62	-2.87492
0.14	-0.11093	0.64	-3.05320
0.16	-0.14969	0.66	-3.23141
0.18	-0.19480	0.68	-3.40819
0.20	-0.24646	0.70	-3.58231
0.22	-0.30482	0.72	-3.75207
0.24	-0.37003	0.74	-3.91584
0.26	-0.44220	0.76	-4.07163
0.28	-0.52144	0.78	-4.21738
0.30	-0.60783	0.80	-4.35076
0.32	-0.70140	0.82	-4.46905
0.34	-0.80217	0.84	-4.56957
0.36	-0.91014	0.86	-4.64910
0.38	-1.02523	0.88	-4.70409
0.40	-1.14737	0.90	-4.73091
0.42	-1.27640	0.92	-4.72521
0.44	-1.41215	0.94	-4.68266
0.46	-1.55438	0.96	-4.59770
0.48	-1.70277	0.98	-4.46546
0.50	-1.85699	1.00	-4.27946

PVT data for CO<sub>2</sub>

$$T^* = 0.2$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	-0.00148	0.52	-1.83975
0.04	-0.00118	0.54	-1.98748
0.06	-0.00874	0.56	-2.13811
0.08	-0.02137	0.58	-2.29082
0.10	-0.03934	0.60	-2.44477
0.12	-0.06283	0.62	-2.59886
0.14	-0.09200	0.64	-2.75197
0.16	-0.12705	0.66	-2.90284
0.18	-0.16815	0.68	-3.04993
0.20	-0.21546	0.70	-3.19175
0.22	-0.26911	0.72	-3.32638
0.24	-0.32922	0.74	-3.45192
0.26	-0.39587	0.76	-3.56604
0.28	-0.46914	0.78	-3.66637
0.30	-0.54905	0.80	-3.75022
0.32	-0.63562	0.82	-3.81438
0.34	-0.72882	0.84	-3.85578
0.36	-0.82857	0.86	-3.87060
0.38	-0.93479	0.88	-3.85474
0.40	-1.04732	0.90	-3.80387
0.42	-1.16596	0.92	-3.71294
0.44	-1.29044	0.94	-3.57667
0.46	-1.42049	0.96	-3.38864
0.48	-1.55569	0.98	-3.14282
0.50	-1.69562	1.00	-2.83146



$$T^* = 0.3$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.03402	0.52	-1.765608
0.04	0.003072	0.54	-1.909818
0.06	-0.00198	0.56	-2.05632
0.08	-0.011904	0.58	-2.204058
0.10	-0.02694	0.60	-2.3517
0.12	-0.047196	0.62	-2.498166
0.14	-0.072954	0.64	-2.641728
0.16	-0.1044	0.66	-2.780712
0.18	-0.141696	0.68	-2.912712
0.20	-0.1851	0.70	-3.0366
0.22	-0.234762	0.72	-3.148632
0.24	-0.290736	0.74	-3.24675
0.26	-0.353418	0.76	-3.327204
0.28	-0.422772	0.78	-3.386682
0.30	-0.49896	0.80	-3.42096
0.32	-0.582048	0.82	-3.425304
0.34	-0.67218	0.84	-3.394692
0.36	-0.769176	0.86	-3.323298
0.38	-0.873354	0.88	-3.204696
0.40	-0.98436	0.90	-3.03102
0.42	-1.101114	0.92	-2.794224
0.44	-1.226808	0.94	-2.484984
0.46	-1.354608	0.96	-2.08944
0.48	-1.487376	0.98	-1.58613
0.50	-1.6245	1.00	-1.0413

$$T^* = 0.4$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.005336	0.52	-1.560208
0.04	0.007328	0.54	-1.684368
0.06	0.004776	0.56	-1.81216
0.08	-0.002464	0.58	-1.935576
0.10	-0.01456	0.60	-2.05656
0.12	-0.031632	0.62	-2.17372
0.14	-0.053928	0.64	-2.285312
0.16	-0.081536	0.66	-2.388936
0.18	-0.114624	0.68	-2.482816
0.20	-0.15336	0.70	-2.56396
0.22	-0.197912	0.72	-2.62944
0.24	-0.248352	0.74	-2.676136
0.26	-0.304824	0.76	-2.700128
0.30	-0.36736	0.78	-2.69724
0.32	-0.51072	0.80	-2.66272
0.34	-0.5916	0.82	-2.587592
0.36	-0.678672	0.84	-2.483792
0.38	-0.7714	0.86	-2.305832
0.40	-0.86992	0.88	-2.097216
0.42	-0.974232	0.90	-1.83384
0.44	-1.082752	0.92	-1.500704
0.46	-1.197288	0.94	-1.108072
0.48	-1.314432	0.96	-0.638976
0.50	-1.4362	0.98	-0.08624
		1.00	+0.554

$$T^* = 0.5$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.00726	0.52	-1.35226
0.04	0.01158	0.54	-1.45611
0.06	0.01152	0.56	-1.5582
0.08	0.00696	0.58	-1.65909
0.10	-0.0022	0.60	-1.7535
0.12	-0.01614	0.62	-1.785
0.14	-0.03493	0.64	-1.92352
0.16	-0.058732	0.66	-1.99584
0.18	-0.08775	0.68	-2.05326
0.20	-0.1219	0.70	-2.0965
0.22	-0.16148	0.72	-2.1186
0.24	-0.20652	0.74	-2.12084
0.26	-0.25615	0.76	-2.09722
0.28	-0.31276	0.78	-2.0455
0.30	-0.37425	0.80	-1.9564
0.32	-0.4408	0.82	-1.83516
0.34	-0.51323	0.84	-1.66782
0.36	-0.58914	0.86	-1.45641
0.38	-0.61279	0.88	-1.18448
0.40	-0.7592	0.90	-0.86805
0.42	-0.85071	0.92	-0.47564
0.44	-0.94572	0.94	-0.02162
0.46	-0.10442	0.96	0.5188
0.48	-1.14504	0.98	1.12945
0.50	-1.24825	1.00	1.839

$$T^* = 0.6$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.00919	0.52	-1.13236
0.04	0.01584	0.54	-1.21300
0.06	0.01824	0.56	-1.29093
0.08	0.01634	0.58	-1.36483
0.10	0.01008	0.60	-1.43328
0.12	-0.00069	0.62	-1.49462
0.14	-0.01604	0.64	-1.54707
0.16	-0.03612	0.66	-1.58858
0.18	-0.06096	0.68	-1.61688
0.20	-0.09069	0.70	-1.62952
0.22	-0.12535	0.72	-1.62364
0.24	-0.16494	0.74	-1.59619
0.26	-0.20951	0.76	-1.54370
0.28	-0.25901	0.78	-1.46237
0.30	-0.31307	0.80	-1.34801
0.32	-0.37250	0.82	-1.19595
0.34	-0.43538	0.84	-1.00058
0.36	-0.50233	0.86	-0.75663
0.38	-0.57304	0.88	-0.45733
0.40	-0.64714	0.90	-0.09580
0.42	-0.72417	0.92	+0.33623
0.44	-0.80363	0.94	0.84722
0.46	-0.88493	0.96	1.46155
0.48	-0.96736	0.98	2.12607
0.50	-1.05013	1.00	2.97015

$$T^* = 0.7$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.01111	0.52	-0.95550
0.04	0.02008	0.54	-1.01939
0.06	0.02496	0.56	-1.07913
0.08	0.02573	0.58	-1.13333
0.10	0.02234	0.60	-1.18041
0.12	0.01473	0.62	-1.21857
0.14	0.00275	0.64	-1.24583
0.16	-0.01356	0.66	-1.26003
0.18	-0.03440	0.68	-1.25861
0.20	-0.05970	0.70	-1.23897
0.22	-0.08948	0.72	-1.19795
0.24	-0.12388	0.74	-1.13226
0.26	-0.16262	0.76	-1.03811
0.28	-0.20579	0.78	-0.91136
0.30	-0.25328	0.80	-0.74745
0.32	-0.30485	0.82	-0.54109
0.34	-0.36026	0.84	-0.28678
0.36	-0.41933	0.86	0.02704
0.38	-0.48145	0.88	0.38423
0.40	-0.54709	0.90	0.83317
0.42	-0.61373	0.92	1.34806
0.44	-0.68193	0.94	1.89765
0.46	-0.75004	0.96	2.56773
0.48	-0.82028	0.98	3.27639
0.50	-0.88876	1.00	4.12241

$$T^* = 0.8$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.01304	0.52	-0.77865
0.04	0.02433	0.54	-0.82577
0.06	0.03167	0.56	-0.86734
0.08	0.03510	0.58	-0.90183
0.10	0.03459	0.60	-0.92755
0.12	0.03008	0.62	-0.94251
0.14	0.02152	0.64	-0.94461
0.16	0.00885	0.66	-0.93146
0.18	-0.00796	0.68	-0.90034
0.20	-0.02886	0.70	-0.84842
0.22	-0.05396	0.72	-0.77103
0.24	-0.08309	0.74	-0.67135
0.26	-0.11625	0.76	-0.52887
0.28	-0.15319	0.78	-0.36433
0.30	-0.19399	0.80	-0.15533
0.32	-0.23825	0.82	0.09627
0.34	-0.28572	0.84	0.39488
0.36	-0.33611	0.86	0.74577
0.38	-0.38902	0.88	1.15446
0.40	-0.44394	0.90	1.62679
0.42	-0.50053	0.92	2.16274
0.44	-0.55744	0.94	2.79446
0.46	-0.61497	0.96	3.46770
0.48	-0.67221	0.98	4.28143
0.50	-0.72544	1.00	5.13329

$$T^* = 0.9$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.01496	0.52	-0.59851
0.04	0.02856	0.54	-0.62990
0.06	0.03837	0.56	-0.65265
0.08	0.04445	0.58	-0.66912
0.10	0.04680	0.60	-0.67434
0.12	0.04539	0.62	-0.66714
0.14	0.04021	0.64	-0.64574
0.16	0.03119	0.66	-0.60746
0.18	0.01836	0.68	-0.54789
0.20	0.00174	0.70	-0.47103
0.22	-0.01862	0.72	-0.36108
0.24	-0.04266	0.74	-0.23130
0.26	-0.07020	0.76	-0.05908
0.28	-0.10121	0.78	0.13980
0.30	-0.13537	0.80	0.38418
0.32	-0.17244	0.82	0.67261
0.34	-0.21222	0.84	1.00986
0.36	-0.25406	0.86	1.40087
0.38	-0.29744	0.88	1.85088
0.40	-0.34294	0.90	2.36741
0.42	-0.38880	0.92	2.94752
0.44	-0.43424	0.94	3.62095
0.46	-0.47889	0.96	4.35860
0.48	-0.52260	0.98	5.19272
0.50	-0.56190	1.00	6.12930

$$T^* = 1.0$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.02	0.01688	0.52	-0.42354
0.04	0.03280	0.54	-0.43810
0.06	0.04507	0.56	-0.44425
0.08	0.05379	0.58	-0.44214
0.10	0.05900	0.60	-0.42753
0.12	0.06067	0.62	-0.39982
0.14	0.05883	0.64	-0.35593
0.16	0.05344	0.66	-0.29320
0.18	0.04455	0.68	-0.21199
0.20	0.03221	0.70	-0.10497
0.22	0.01649	0.72	0.02961
0.24	-0.00250	0.74	0.19311
0.26	-0.02460	0.76	0.38732
0.28	-0.04962	0.78	0.62861
0.30	-0.07732	0.80	0.90049
0.32	-0.10741	0.82	1.22417
0.34	-0.13960	0.84	1.59828
0.36	-0.17317	0.86	2.02764
0.38	-0.20815	0.88	2.51375
0.40	-0.24378	0.90	3.07188
0.42	-0.27864	0.92	3.70504
0.44	-0.31333	0.94	4.41309
0.46	-0.34602	0.96	5.19052
0.48	-0.37603	0.98	6.09348
0.50	-0.40185	1.00	7.05255



PVT DATA FOR CO<sub>2</sub>

$$T^* = 2.0$$

$$T^* = 3.0$$

DENSITY $\rho^*$	PRESSURE $P^*$	DENSITY $\rho^*$	PRESSURE $P^*$
0.10	0.18	0.10	0.30
0.20	0.328	0.20	0.624
0.30	0.480	0.30	1.008
0.40	0.688	0.40	1.56
0.50	1.06	0.50	2.37
0.60	1.776	0.60	3.708
0.70	3.08	0.70	5.796
0.80	5.344	0.80	9.072
0.90	9.072	0.90	14.256
1.00	14.92	1.00	22.2
1.10	23.76	1.10	34.254
1.20	37.152	1.20	52.704
1.30	58.188	1.30	80.652
1.40	90.44	1.40	123.48

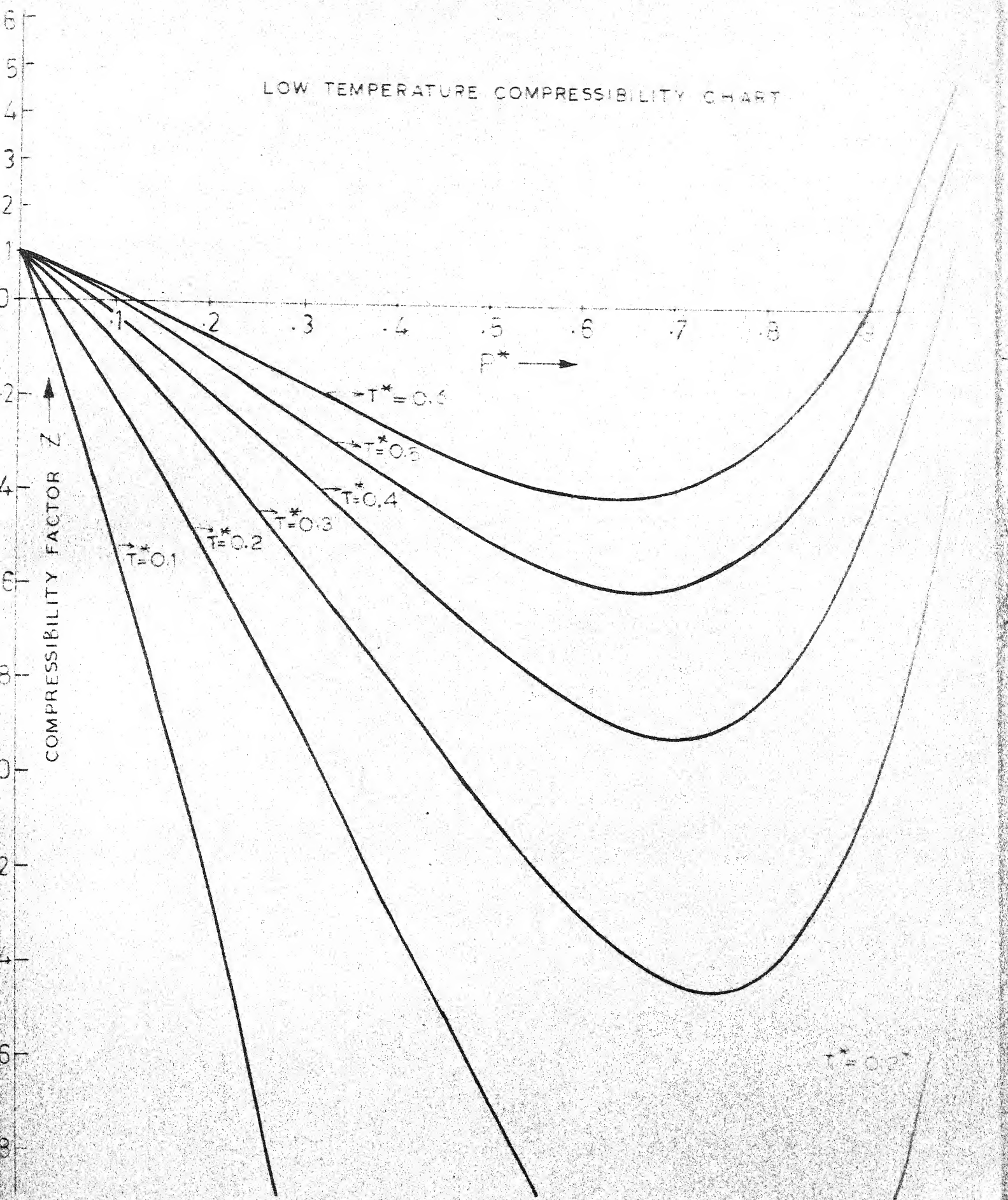


Fig.3 Equation of state for  $\text{CO}_2$

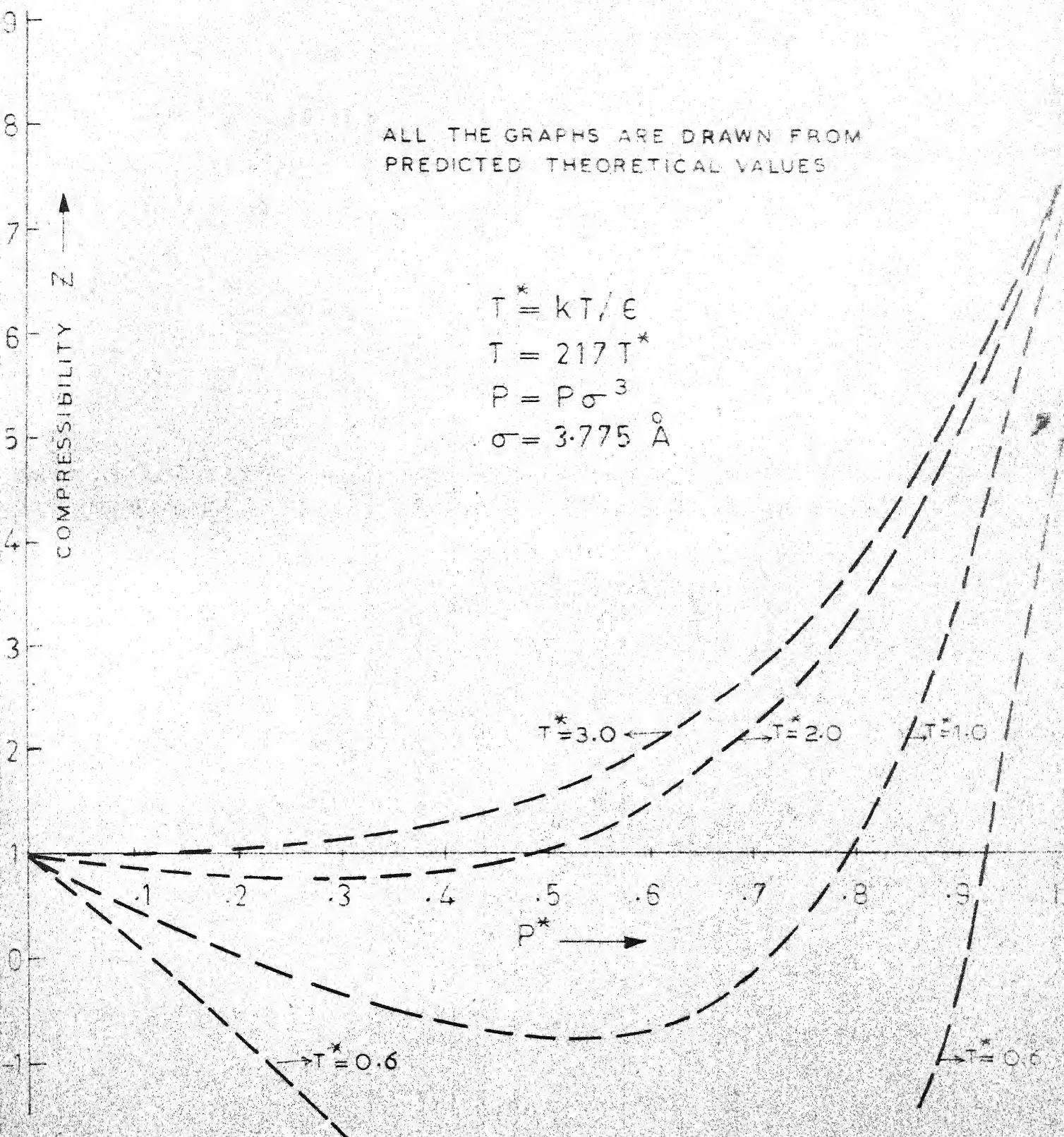
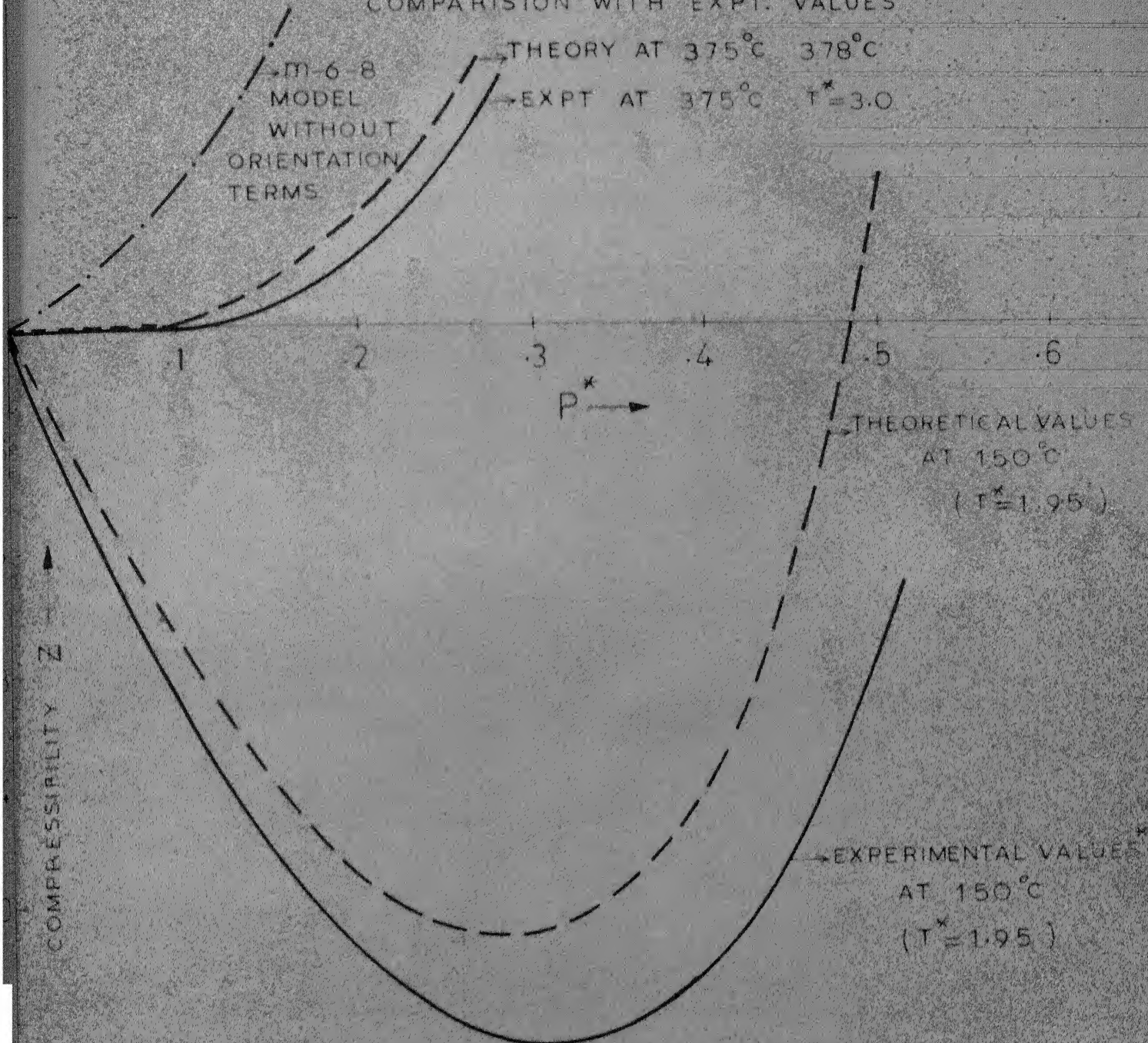


Fig.4 Equation of state for  $\text{CO}_2$



# COMPARISON WITH EXPT. VALUES



EXPERIMENTAL VALUES AVAILABLE ONLY UP TO  $P^* = .5132$   
WHICH CORRESPONDS TO 500 ATMOSPHERIC PRESSURE  
AT 150°C

IND. ENG. CHEM. 39, 517 (1947)

AT 375°C EXPERIMENTAL VALUES AVAILABLE UP TO  
500 ATA WHICH GIVES  $P^* = .2814$

Fig. 5 Equation of state for CO<sub>2</sub>

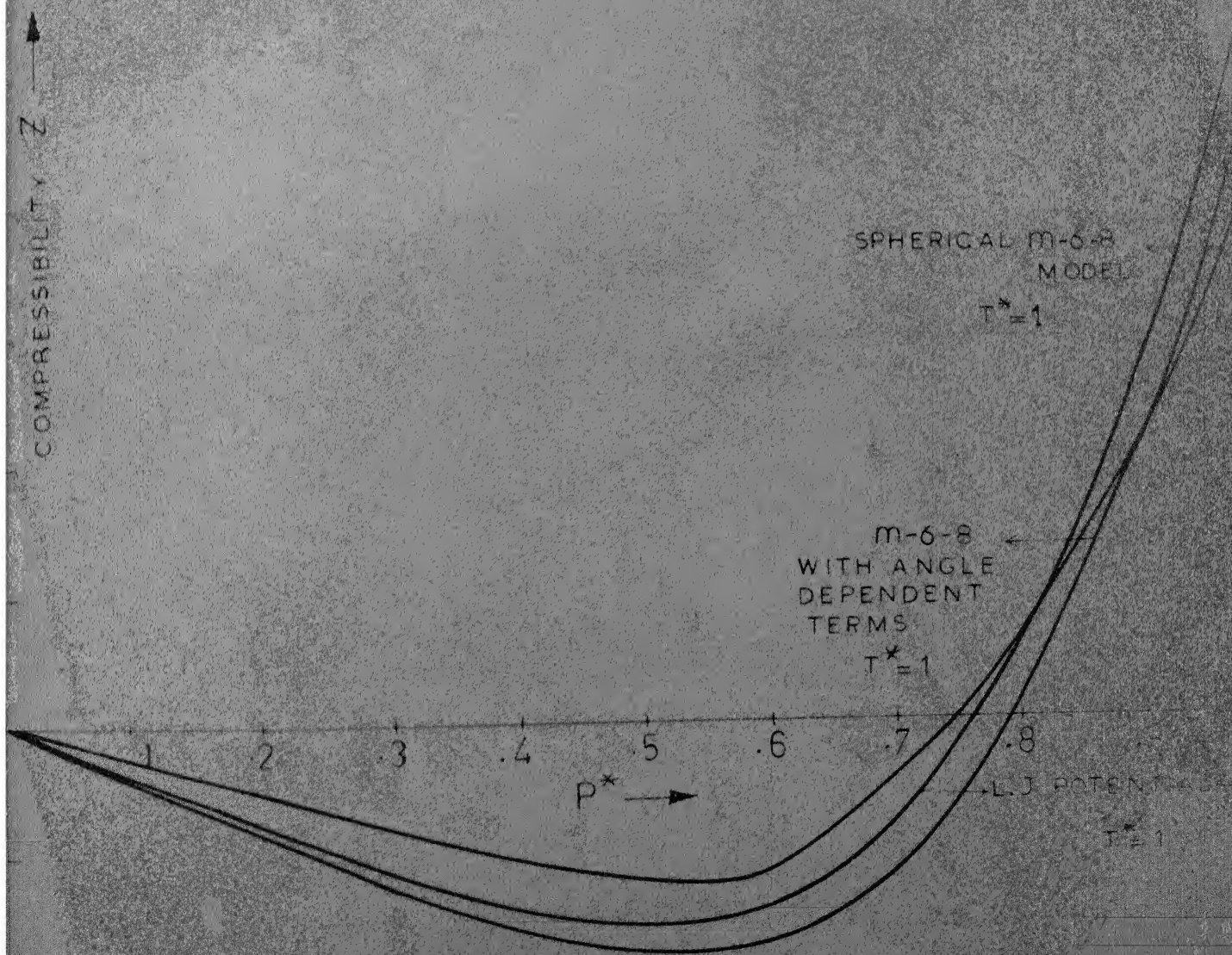


Fig.6 Comparison with other models



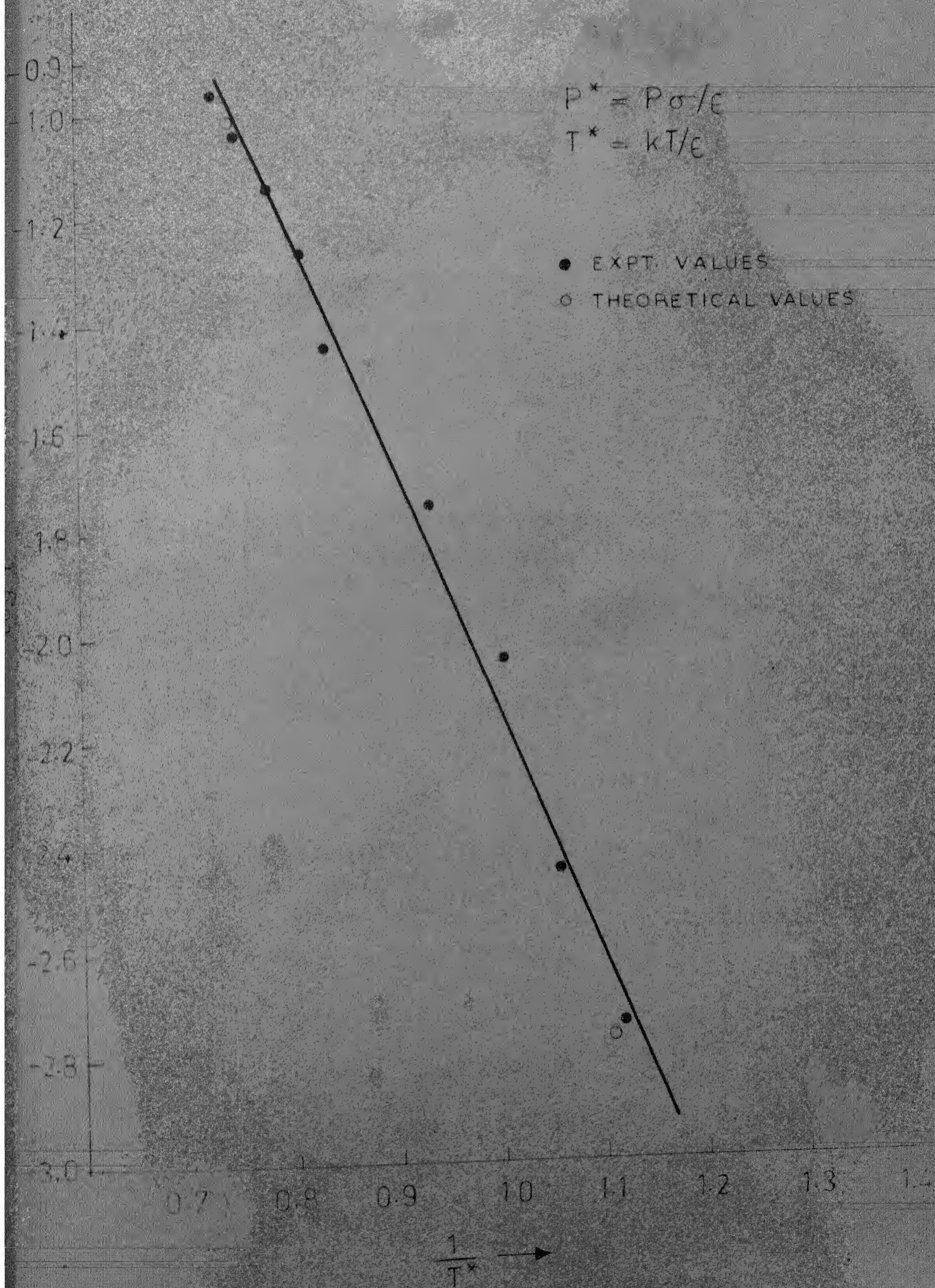


Fig.8. Comparision of vapour pressure data

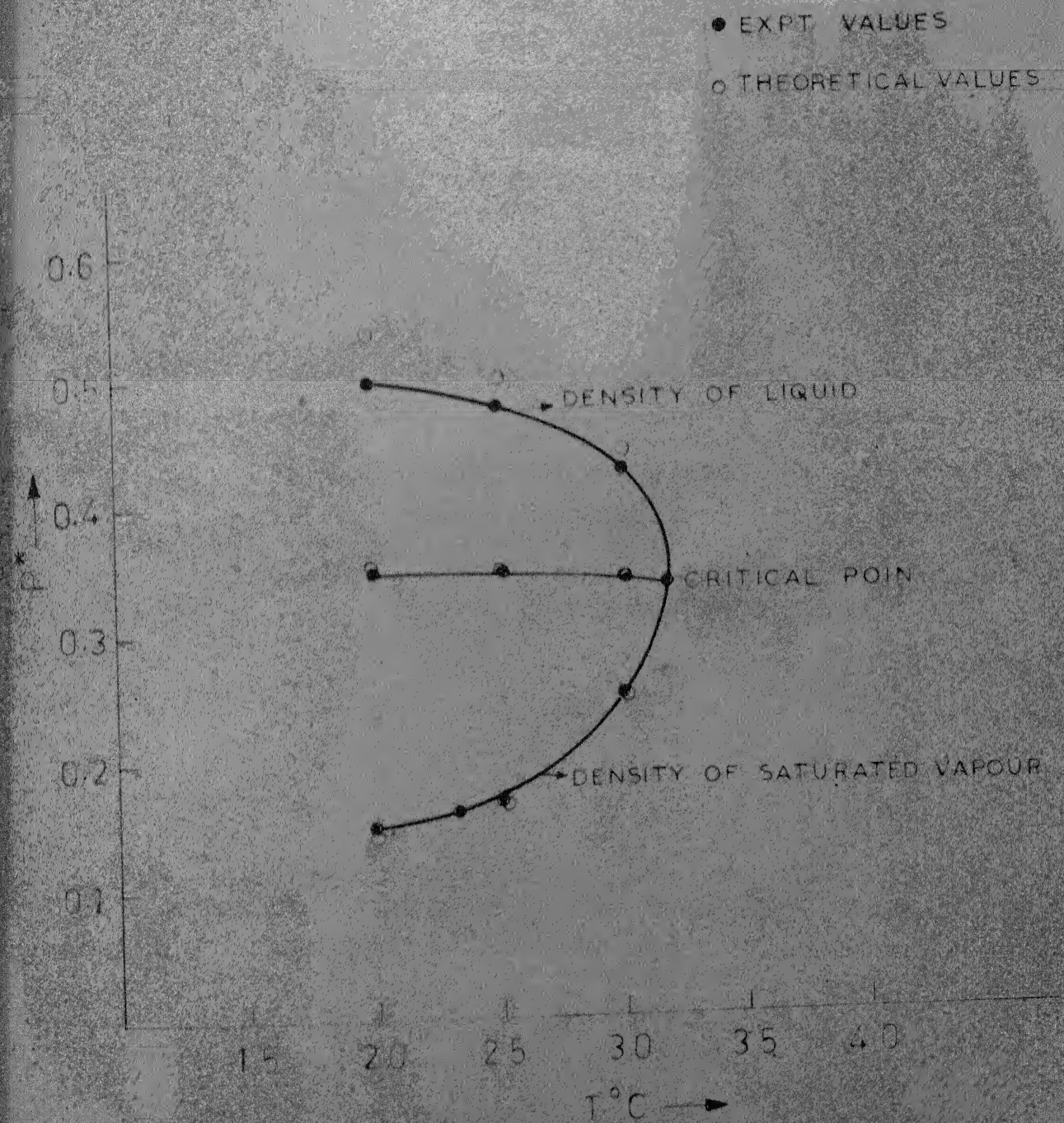


Fig. 2. Vapour-liquid equilibrium for CO<sub>2</sub>

**A 59502**

This book is to be returned on the date last stamped.

This image shows a blank sheet of white paper with horizontal ruling lines. A single vertical line runs down the center of the page, creating two equal-width columns. The horizontal lines are evenly spaced and extend across the entire width of the paper. There is no handwriting or other markings on the page.

CHE-1979-M-ANT-VAR